

IAP20 Rec'd PCT/PTO 30 DEC 2005

METAL OXIDE FORMULATIONS

The present invention relates to metal oxide formulations and especially UV screen compositions including those suitable for cosmetic and topical pharmaceutical use containing such oxides as well as polymeric compositions containing the same.

The effects associated with exposure to sunlight are well known. Thus exposure of the skin to UVA and UVB light may result in, for example, sunburn, premature ageing and skin cancer.

Commercial sunscreens generally contain components which are able to reflect and/or absorb UV light. These components include, for example, inorganic oxides such as zinc oxide and titanium dioxide as well as organic sunscreen agents.

Most organic sunscreen agents absorb light over only a part of the UVA-UVB spectrum with the result that if one is to obtain a screening effect covering the whole UVA-UVB spectrum it is generally necessary to use a combination of different organic sunscreen agents. Some organic sunscreen agents and other components of sunscreen compositions are stable to UV light but others are photosensitive and/or may after being excited by UV light degrade another ingredient of the composition.

Titanium dioxide and zinc oxide are generally formulated as "micronised" or "ultrafine" (20-50 nm) particles (so-called microreflectors) because particles whose size is less than 10% of the wavelength of the incident light scatter light according to Rayleigh's Law, whereby the intensity of scattered light is inversely proportional to the fourth power of the wavelength. Consequently, they scatter UVB light (with a wavelength of from 280 or 290 to 315/ 320 nm) and UVA light (with a wavelength of from 315/320 to 400 nm) more than the longer, visible wavelengths, preventing sunburn whilst remaining invisible on the skin.

However, titanium dioxide and zinc oxide also absorb UV light efficiently, leading via the initial formation of electron hole pairs to the formation of superoxide and hydroxyl radicals and which may in turn initiate damage to other components of the composition. The crystalline forms of TiO_2 , anatase and rutile, are semiconductors with band gap energies of about 3.23 and 3.06 eV respectively, corresponding to light of about 385 nm and 400 nm (1 eV corresponds to 8066 cm^{-1}).

-2-

Thus these oxides while providing good wavelength cover can enhance the degradation of organic sunscreen agents, including UVA organic sunscreens, for example oxybenzone as well as cause degradation of other components of the formulation. Attempts have been made to reduce the adverse effects of TiO₂ and
5 ZnO by coating, but coatings are not invariably effective.

It has now surprisingly been found, according to the present invention, that the degradation of any compound which is adversely affected by TiO₂ and/or ZnO, and especially of organic sunscreen agents, can be retarded if the compositions containing them contain zinc oxide or titanium dioxide which has been doped with
10 another element and/or reduced zinc oxide in addition to, or instead of, the "ordinary" TiO₂ and/or ZnO. In other words by using, in a sunscreen composition etc., these doped or reduced materials rather than ordinary titanium dioxide or zinc oxide alone it is, for example, possible either to provide a composition which gives better protection against UV light for the same quantity of organic sunscreen agent or a
15 composition having the same screening effect against UV light but containing a smaller quantity of organic sunscreen agent. Indeed it is possible to provide all day protection sunscreens by incorporating the doped and/or reduced materials.

Accordingly the present invention provides a composition which comprises at least one ingredient which is adversely affected by the presence of TiO₂ and/or ZnO
20 (usually of course the adverse effect will be brought about by UV light in the presence of TiO₂ and/or ZnO), and TiO₂ and/or ZnO which has been doped with another element and/or reduced zinc oxide.

Whether or not an adverse effect occurs, and under what conditions, will in general be clear to the person skilled in the art in the given context. Whether or not
25 an effect is adverse, and the conditions that are relevant, might well be different for different products and for different end uses. For example, for sunscreens and other compositions for cosmetic and topical use on the body, one might be concerned with adverse effects to ingredients that arise when the composition is subjected for say 8 hours to UV light of a wavelength from 290 to 400 nm at an intensity corresponding
30 to midday Mediterranean sunlight, or say an intensity of 10 mW per square cm. and

-3-

in the presence of TiO_2 and/or ZnO . In the case of compositions that are not used on the body, such as paints and coatings, adverse effects on ingredients that become apparent only after exposure of the composition over longer periods of time (for example one week, one month or one year), or under harsher conditions, might well
5 be of concern. In preferred embodiments we are concerned with ingredients that undergo any chemical change (generally a chemical change that renders the composition less functionally effective, or that reduces its useful life) when subjected to the conditions referred to above.

Components which are adversely affected by TiO_2 and/or ZnO are in general
10 those which are sensitive to free radical attack. They may be intrinsically stable; this attack is related to the homolytic bond dissociation energy. Such components include large molecules such as polymers as well as small molecules such as those with ethylenic unsaturation or those which possess a labile hydrogen atom, for example a tertiary hydrogen atom or other labile species including chlorine. Free
15 radical attack may also break amide or ester linkages of small molecules or of large molecules such as polyamides or polyesters.

The presence of TiO_2 or ZnO may result in a change in a physical property of the component. With a polymer this may be, for example, a change in tensile strength or elongation at break; while with a small molecule, the free radical attack
20 generally results in a change in its chemical structure which gives rise to a change in physical properties such as melting point, boiling point, viscosity, a change in its functional character or, in some cases, toxicity. All these changes can, of course, be measured as one skilled in the art would appreciate.

The present invention has particular applicability for UV sunscreen
25 compositions suitable for cosmetic or pharmaceutical use. By "UV sunscreen composition suitable for cosmetic or topical pharmaceutical use" is meant any cosmetic or topical pharmaceutical composition having UV sunscreen activity i.e. it includes compositions whose principal function may not be suncreening. It will be appreciated that the doped TiO_2/ZnO or reduced ZnO may be the only ingredient of
30 the composition having UV suncreening activity i.e. the composition need not

-4-

necessarily contain an organic UV sunscreen agent. However the composition will contain an ingredient which is adversely affected by TiO_2 and/or ZnO . It is to be understood that the composition can also contain TiO_2 and/or ZnO which has not been doped or reduced.

- 5 The organic component which may be degraded is generally a UV sunscreen agent. Certain components, typically organic sunscreen agents, when exposed to UV light, are substantially stable to this light but are degraded when exposed to UV light in the presence of titanium dioxide or zinc oxide. Accordingly a full spectrum sunscreen agent cannot be satisfactorily formulated using such a combination. If,
- 10 however, a doped titanium dioxide or a doped or reduced zinc oxide is used (partially or completely) instead of ordinary TiO_2/ZnO the organic sunscreen agent is not degraded in the same way. Thus the present invention also provides a method of increasing the UV spectrum of a sunscreen formulation which comprises an organic sunscreen agent which is adversely affected by UV light in the presence of titanium
- 15 dioxide and/or zinc oxide which comprises incorporating in the formulation doped TiO_2 and/or doped or reduced ZnO , as well as a composition which comprises an organic sunscreen agent which is adversely affected by UV light (in the presence of undoped TiO_2 and/or ZnO) and doped TiO_2 and/or doped or reduced ZnO .

- In a preferred embodiment the composition has a rate of loss of UV
- 20 absorption due to free radical attack derived from TiO_2 and/or ZnO which is less, preferably at least 5% less, than that of a composition having the same formulation except that it does not contain the said TiO_2 and/or ZnO which has been doped with another element or reduced zinc oxide. Thus if the rate of loss of UV absorption (during UV exposure) over at least a proportion of the UVA and/or UVB spectrum is
- 25 X then the amount of the organic component(s) which is degraded possesses a said rate of loss of Y where Y is greater than X, preferably by at least 5%, and the amount of doped TiO_2 and/or ZnO and/or reduced zinc oxide reduces the said rate of loss from Y to X. The present invention also provides the use of a doped TiO_2/ZnO or reduced zinc oxide to reduce the rate of loss in UV absorption of a sunscreen
- 30 composition containing one or more organic UV sunscreen agents which are

-5-

adversely affected by TiO_2 and/or ZnO . The present invention further provides a method of increasing the effectiveness (improving the stability) of an organic suncreening composition which comprises one or more components which are degraded by UV light in the presence of TiO_2 and/or ZnO which comprises

- 5 incorporating into the composition a doped TiO_2/ZnO and/or reduced zinc oxide. Sometimes the degradation products (breakdown chemicals) are toxic. Accordingly, the present invention also provides a method of reducing the production of toxic compounds in a UV sunscreen composition which comprises incorporating therein a doped TiO_2/ZnO and/or reduced ZnO .

- 10 However, other organic components may also be susceptible to free radical attack, the degraded products that result potentially causing degradation of the UV sunscreen agent.

- However, it should be noted that this principle may be applied to compositions other than cosmetics. Where there is present within the composition a
15 specific organic component which is not degraded by UV light, but which is degraded by free radical attack when in contact with TiO_2 and/or ZnO in the presence of UV light, the change in that organic component may be followed by determining a change in one or more physical properties of the composition. Techniques specific to the physical property may be used to follow the change. Such physical properties
20 may include viscosity, melting range and boiling range.

- The rate of loss of absorption can be determined by illuminating a sample of the composition with and without the doped TiO_2 and/or ZnO of defined thickness with UV light of the appropriate wavelength, and determining the absorption of UV light by the composition over a given period, typically 60 minutes, obtaining a plot
25 over that period for the wavelengths in question and determining the area under the curve, from which the rate of loss can be calculated. Clearly the smaller the area under the curve the smaller the loss. For UVA absorption wavelengths from 320 to 400, especially from 340 to 390 nm, are considered.

- While any reduction in the loss of UV absorption is an advantage, it is
30 generally desirable that the presence of the doped oxide should reduce the rate of UV

-6-

absorption by an amount of at least a 5%, preferably at least 10%, more preferably at least 15%, especially at least 20% and most preferably at least 40%.

The compositions of the present invention for cosmetics use may be, for example, lipsticks, skin anti-ageing compositions in the form of, for example, 5 creams, including anti-wrinkle formulations, exfoliating preparations including scrubs, creams and lotions, skin lightening compositions in the form of, for example, face powders and creams, preparations for the hands including creams and lotions, moisturising preparations, compositions for protecting the hair such as conditioners, shampoos and hair lacquers as well as hair masks and gels, skin cleansing 10 compositions including wipes, lotions and gels, eye shadow and blushers, skin toners and serums as well as washing products such as shower gels, bath products including bubble baths, bath oils, but, preferably, sunscreens. In this connection we should point out that the expression "cosmetic UV sunscreen composition", as used herein, includes any composition applied to the skin which may leave a residue on the skin 15 such as some washing products. Compositions of the present invention may be employed as any conventional formulation providing protection from UV light. The composition may also be a pharmaceutical composition suitable for topical application. Such compositions are useful, in particular, for patients suffering from disorders of the skin which are adversely affected by UV light such as those giving 20 rise to polymorphous light eruptions.

Organic sunscreen agents which can be used in the compositions of the present invention include any conventional sunscreen agent which gives protection against UV light while if there is no other component which is degraded by TiO_2 and/or ZnO the sunscreen agent is itself degraded by TiO_2 and/or ZnO . Suitable 25 sunscreen agents are listed in the IARC Handbook of Cancer Prevention, vol. 5, Sunscreens, published by the International Agency for Research on Cancer, Lyon, 2001 and include:

- (a) Para-aminobenzoic acids (PABA), (UVB absorbers) esters and derivatives thereof, for example amyldimethyl-; 30 ethyldihydroxypropyl-; ethylhexyl dimethyl-; ethyl-; glyceryl-; and 4-

-7-

bis-(polyethoxy)- PABA.

- (b) Cinnamates (UVB) especially esters including methyl cinnamate esters and methoxycinnamate esters such as octylmethoxy cinnamate, ethyl methoxycinnamate, especially 2-ethylhexyl para-methoxycinnamate, isoamyl p-methoxy cinnamate, or a mixture thereof with diisopropyl cinnamate, 2-ethoxyethyl -4-methoxycinnamate, DEA-methoxycinnamate (diethanolamine salt of para-methoxy hydroxycinnamate) or α,β -di-(para-methoxycinnamoyl)- α' -(2-ethylhexanoyl)-glycerin, as well as diisopropyl methylcinnamate;
- (c) benzophenones (UVA) such as 2,4-dihydroxy-; 2-hydroxy-4-methoxy; 2,2'-dihydroxy-4,4'-dimethoxy-; 2,2'-dihydroxy-4-methoxy-; 2,2',4,4'-tetrahydroxy-; and 2-hydroxy-4-methoxy-4'-methyl-benzophenones, benzenesulphonic acid and its sodium salt; sodium 2,2'-dihydroxy-4,4'-dimethoxy-5-sulphobenzophenone and oxybenzone;
- (d) dibenzoylmethanes (UVA) such as butyl methoxydibenzoyl methane, especially 4-tert-butyl-4'methoxydibenzoylmethane;
- (e) 2-phenylbenzimidazole-5 sulfonic acid UVB and phenyldibenzimidazole sulfonic acid and their salts;
- (f) alkyl- β,β -diphenylacrylates (UVB) for example alkyl α -cyano- β,β -diphenylacrylates such as octocrylene;
- (g) triazines (UVB) such as 2,4,6-trianilino-(p-carbo-2-ethyl-hexyl-1-oxy)-1,3,5 triazine as well as octyl triazone e.g. ethylhexyltriazone and diethylhexyl butamido triazone.
- (h) camphor derivatives (generally UVB) such as 4-methylbenzylidene and 3-benzylidene- camphor and terephthalylidene dicamphor sulphonic acid (UVA), benzylidene camphor sulphonic acid, camphor benzalkonium methosulphate and polyacrylamidomethyl benzylidene camphor;
- (i) organic pigment suncreening agents such as methylene bis-benzotriazole tetramethyl butylphenol;

-8-

- (j) silicone based sunscreens agents such as dimethicodiethyl benzal malonate.
- (k) salicylates (UVB) such as dipropylene glycol-, ethylene glycol-, ethylhexyl-, isopropylbenzyl-, methyl-, phenyl-, 3,3,5-trimethyl- and TEA-salicylate (compound of 2-hydroxybenzoic acid and 2,2'2"-nitrilotris (ethanol));
- (l) anthranilates (UVA) such as menthyl anthranilate as well as bisimidazylate (UVA), dialkyl trioleate (UVB), 5-methyl-2-phenylbenzoxazole (UVB) and urocanic acid (UVB).

10 Some compounds are effective for both UVA and UVB. These include anisotriazine, methylene bisbenzotriazolyl tetramethylbutyl-phenol and drometrizole trisiloxane (Mexoryl XL).

The organic sunscreen agent(s) are typically present in the compositions at a concentration from 0.1 to 20%, preferably 1 to 10%, and especially 2 to 5%, by weight based on the weight of the composition.

In the compositions, which are generally aqueous, the metal oxides are preferably present at a concentration of about 0.5 to 20 % by weight, preferably about 1 to 10 % by weight and more preferably about 3 to 8 % by weight, in particular about 4 to 7%, such as 4 to 6% for example about 5%, by weight.

20 The compositions may be in the form of, for example, lotions, typically with a viscosity of 4000 to 10,000 mPas, e.g. thickened lotions, gels, vesicular dispersions, creams, typically a fluid cream with a viscosity of 10,000 to 20,000 mPas or a cream of viscosity 20,000 to 100,000 mPas, milks, powders, solid sticks, and may be optionally packaged as aerosols and provided in the form of foams or sprays.

25 The compositions may contain any of the ingredients used in such formulations including fatty substances, organic solvents, silicones, thickeners, liquid and solid emollients, demulcents, other UVA, UVB or broad-band sunscreen agents, antifoaming agents, antioxidants such as butyl hydroxy toluene, buffers such as lactic acid with a base such as triethanolamine or sodium hydroxide, plant extracts such as
30 Aloe vera, cornflower, witch hazel, elderflower and cucumber, activity enhancers,

-9-

moisturizing agents, and humectants such as glycerol, sorbitol, 2-pyrrolidone-5-carboxylate, dibutylphthalate, gelatin and polyethylene glycol, perfumes, preservatives, such as para-hydroxy benzoate esters, surface-active agents, fillers and thickeners, sequesterants, anionic, cationic, nonionic or amphoteric polymers or mixtures thereof, propellants, alkalizing or acidifying agents, colorants and powders, including metal oxide pigments with a particle size of from 100 nm to 20000 nm such as iron oxides along with conventional (undoped) TiO₂ and ZnO.

Other ingredients of cosmetic compositions, for example some surface-active agents may have the effect of degrading certain sunscreen agents in the presence of UV light. Also TiO₂ and ZnO are known to degrade certain organic sunscreens such as oxybenzone as well as antioxidants such as vitamins e.g. vitamins A, B, C and E, and also anti-ageing factors such as niacinamide, retinoids and coenzyme MEQ10 etc. It will be appreciated that it is particularly useful to use the doped TiO₂ and/or ZnO and/or reduced ZnO with such sunscreens. This is because TiO₂ and ZnO do generally have a positive UV absorptive effect. Thus by using the doped TiO₂ and/or ZnO and/or reduced ZnO it may be possible to use less antioxidant or make the formulation longer lasting.

The organic solvents are typically selected from lower alcohols and polyols such as ethanol, isopropanol, propylene glycol, glycerin and sorbitol as well as methylene chloride, acetone, ethylene glycol monoethyl ether, diethylene glycol monobutyl ether, diethylene glycol mono-ethyl, ether, dimethyl sulphoxide, dimethyl formamide and tetrahydrofuran.

The fatty substances may consist of an oil or wax or mixture thereof, fatty acids, fatty acid esters, fatty alcohols, vaseline, paraffin, lanolin, hydrogenated lanolin or acetylated lanolin, beeswax, ozokerite wax and paraffin wax.

The oils are typically selected from animal, vegetable, mineral or synthetic oils and especially hydrogenated palm oil, hydrogenated castor oil, vaseline oil, paraffin oil, Purcellin oil, silicone oil such as polydimethyl siloxanes and isoparaffin.

The waxes are typically animal, fossil, vegetable, mineral or synthetic waxes. Such waxes include beeswax, Carnauba, Candelilla, sugar cane or Japan waxes,

-10-

ozokerites, Montan wax, microcrystalline waxes, paraffins or silicone waxes and resins.

The fatty acid esters are, for example, isopropyl myristate, isopropyl adipate, isopropyl palmitate, octyl palmitate, C₁₂-C₁₅ fatty alcohol benzoates ("FINSOLV TN" from FINETEX), oxypropylenated myristic alcohol containing 3 moles of propylene oxide ("WITCONOL APM" from WITCO), capric and caprylic acid triglycerides ("MIGLYOL 812" from HULS).

The compositions may also contain thickeners such as cross-linked or non cross-linked acrylic acid polymers, and particularly polyacrylic acids which are cross-linked using a polyfunctional agent, such as the products sold under the name "CARBOPOL" by the company GOODRICH, cellulose or derivatives thereof such as methylcellulose, hydroxymethylcellulose, hydroxypropyl methylcellulose, sodium salts of carboxymethyl cellulose, or mixtures of cetylstearyl alcohol and oxyethylenated cetylstearyl alcohol containing, say, 33 moles of ethylene oxide.

Desirably, the weight ratio of water-dispersible titanium dioxide to oil-dispersible titanium dioxide is from 1:4 to 4:1, preferably from 1:2 to 2:1 and ideally about equal weight proportions.

Suitable emollients include stearyl alcohol, glyceryl monoricinoleate, mink oil, cetyl alcohol, isopropyl isostearate, stearic acid, isobutyl palmitate, isocetyl stearate, oleyl alcohol, isopropyl laurate, hexyl laurate, decyl oleate, octadecan-2-ol, isocetyl alcohol, eicosanyl alcohol behenyl alcohol, cetyl palmitate, silicone oils such as dimethylpolysiloxane, di-n-butyl sebacate, isopropyl myristate, isopropyl palmitate, isopropyl stearate, butyl stearate, polyethylene glycol, triethylene glycol, lanolin, cocoa butter, corn oil, cotton seed oil, olive oil, palm kernel oil, rapeseed oil, safflower seed oil, evening primrose oil, soybean oil, sunflower seed oil, avocado oil, sesame seed oil, coconut oil, arachis oil, castor oil, acetylated lanolin alcohols, petroleum jelly, mineral oil, butyl myristate, isostearic acid, palmitic acid, isopropyl linoleate, lauryl lactate, myristyl lactate, decyl oleate, myristyl myristate.

Suitable propellants include propane, butane, isobutane, dimethyl ether, carbon dioxide, nitrous oxide.

-11-

Suitable powders include chalk, talc, fullers earth, kaolin, starch, gums, colloidal silica sodium polyacrylate, tetra alkyl and/or trialkyl aryl ammonium smectites, chemically modified magnesium aluminium silicate, organically modified montmorillonite clay, hydrated aluminium silicate, fumed silica, carboxyvinyl
 5 polymer, sodium carboxymethyl cellulose, ethylene glycol monostearate.

When the compositions of the present invention are sunscreens they may be in the form of, for example, suspensions or dispersions in solvents or fatty substances or as emulsions such as creams or milks, in the form of ointments, gels, solid sticks or aerosol foams. The emulsions, which can be oil-in-water or water-in-oil
 10 emulsions, may further contain an emulsifier including anionic, nonionic, cationic or amphoteric surface-active agents; for a water-in-oil emulsion the HLB is typically from 1 to 6 while a larger value i.e greater than 6 is desirable for an oil-in-water emulsion. Generally, water amounts to up to 80%, typically 5 to 80%, by volume. Specific emulsifiers which can be used include sorbitan trioleate, sorbitan tristearate,
 15 glycerol monooleate, glycerol monostearate, glycerol monolaurate, sorbitan sesquioleate, sorbitan monooleate, sorbitan monostearate, polyoxyethylene (2) stearyl ether, polyoxyethylene sorbitol beeswax derivative, PEG 200 dilaurate, sorbitan monopalmitate, polyoxyethylene (3.5) nonyl phenol, PEG 200 monostearate, sorbitan monostearate, sorbitan monolaurate, PEG 400 dioleate, polyoxyethylene (5)
 20 monostearate, polyoxyethylene (4) sorbitan monostearate, polyoxyethylene (4) lauryl ether, polyoxyethylene (5) sorbitan monooleate, PEG 300 monooleate, polyoxyethylene (20) sorbitan tristearate, polyoxyethylene (20) sorbitan trioleate, polyoxyethylene (8) monostearate, PEG 400 monooleate, PEG 400 monostearate, polyoxyethylene (10) monooleate, polyoxyethylene (10) stearyl ether,
 25 polyoxyethylene (10) cetyl ether, polyoxyethylene (9.3) octyl phenol, polyoxyethylene (4) sorbitan monolaurate, PEG 600 monooleate, PEG 1000 dilaurate, polyoxyethylene sorbitol lanolin derivative, polyoxyethylene (12) lauryl ether, PEG 1500 dioleate, polyoxyethylene (14) laurate, polyoxyethylene (20) sorbitan monostearate, polyoxyethylene (20) sorbitan monooleate, polyoxyethylene
 30 (20) stearyl ether, polyoxyethylene (20) sorbitan monopalmitate, polyoxyethylene (20) cetyl ether, polyoxyethylene (25) oxypropylene monostearate, polyoxyethylene

-12-

(20) sorbitol monolaurate, polyoxyethylene (23) lauryl ether, polyoxyethylene (50) monostearate, and PEG 4000 monostearate. Alternatively the emulsifier can be a silicone surfactant, especially a dimethyl polysiloxane with polyoxyethylene and/or polyoxypropylene side chains, typically with a molecular weight of 10,000 to 50,000, especially cyclo-methicone and dimethicone copolyol. They may also be provided in the form of vesicular dispersions of ionic or nonionic amphiphilic lipids prepared according to known processes.

It can be advantageous to use both a water-dispersible and an oil-dispersible titanium dioxide or zinc oxide, at least one of which is doped or, in the case of zinc oxide, reduced. It has been found that when an emulsion is spread on the skin it has a tendency to break down into oily and non-oily areas. When the water evaporates the oil-dispersible particles will tend to be in the oily areas thus leaving areas unprotected. This can be avoided by having both hydrophilic and hydrophobic particles in the emulsion so that some are retained in hydrophilic areas and others in hydrophobic areas.

Water-dispersible particles can be uncoated or coated with a material to impart a hydrophilic surface property to the particles. Examples of such materials include aluminium oxide and aluminum silicate. Oil-dispersible particles which exhibit a hydrophobic surface property, are suitably coated with metal soaps such as aluminium stearate, aluminium laurate or zinc stearate, or with organosilicone compounds.

Although the present invention has particular utility for UV sunscreen compositions which may contain TiO_2 and/or ZnO , it extends to all compositions which may contain TiO_2 and/or ZnO . Thus the present invention also has applicability for polymeric compositions. By "a polymeric composition" as used herein is meant a composition which comprises one or more polymeric materials. The composition can be solid or liquid.

In some instances, the composition of the present invention will contain TiO_2 and/or ZnO which has not been doped or, in the case of ZnO , reduced. Typically such undoped TiO_2/ZnO will be present as pigment, generally having a particle size

-13-

of at least 100 nm.

Typical solid materials include polymeric solids including three dimensional objects, films and fibres as well as textiles and fabrics e.g. clothing and netting made from woven and non-woven fibres as well as foamed articles. Three-dimensional
5 objects include those made by melt-forming processes including extruded and moulded articles. Typical articles to which the present invention may be applied include generally external household and building materials including blinds and plastics curtains, trellises, pipes and guttering, cladding and facings such as soffit board and plastics roofing material which can be profiled as with corrugated
10 sheeting, doors and windows frames. Other articles include advertising hoardings and the like e.g. advertising boards on vehicle sides as well as vehicle bodies and body parts including bumpers for cars, buses and trucks as well as roofs which can be used also for boats, as well as superstructures and hulls for boats and also bodies for lawnmowers and tractors and yachts, along with containers such as bottles, cans,
15 drums, buckets and oil and water storage containers. Other objects include garden furniture.

Films to which the present invention can be applied include self supporting as well as non-self supporting films such as coatings. Self-supporting films to which the present invention applies include photographic films, packaging film and plastic
20 film bearing indicia, typically as advertising film, which can also be applied over advertising hoardings. Such films can contain one or more customary ingredients for such products. Thus photographic film will contain one or more dyes or dye couplers and, optionally, a silver halide.

Coating compositions are typically paints and varnishes which contain a
25 polymer either as the active ingredient as in some varnishes or as a support as in paints along with furniture polishes, waxes and creams; they can be aqueous or non aqueous i.e. contain an organic solvent. This coating composition can be in the form of a waterproofing agent. These coating compositions can contain one or more customary ingredients for such products.

30 The polymers which can be used in the compositions of the present invention

-14-

include natural and synthetic polymers which may be thermoplastic or thermosetting.

The suitable polymers which may be homopolymers or copolymers which can be random, block or graft copolymers; the polymers can be crosslinked. Such polymers may be saturated or unsaturated. Typical polymers include alkylene
5 polymers such as ethylene and propylene polymers, typically homopolymers, including polyethylene foams, including PTFE, siloxane and sulphide polymers, polyamides such as nylon, polyesters, acrylate and methacrylate polymers e.g. poly(methyl methacrylate) as well as PET, polyurethanes, including foams, vinyl
10 polymers such as styrene polymers e.g. ABS, including polystyrene foam vinyl chloride polymers and polyvinyl alcohol. Fluorinated polymers such as PTFE and polyvinylidene fluoride can be used. The polymers can be thermosetting as with epoxy resins as well as phenolic, urea, melamine and polyester resins

Natural polymers which can be used include cellulosic polymers, as in paper including starch, polysaccharides, lignins, and polyisoprenes such as natural rubbers.

15 Typical polymers for different applications include the following: (a) polyester, polyamide e.g. nylon, acrylics for fibres and fabrics; (b) polyester, polyvinyl chloride, polyethylene, polypropylene for bottles and the like; (c) polyethylene, polypropylene, polyvinyl chloride for film (non active such as packaging).

20 The polymeric compositions can contain the usual additional ingredients characteristic for the composition in question including inorganic and organic pigments, including "ordinary" TiO_2 and/or ZnO , fillers and extenders as well as light stabilisers, typically hindered amine stabilisers. The additional ingredients may themselves be susceptible to attack, with the degraded components potentially
25 causing degradation of the polymer or of other components of the composition.

Reference may be made to a "physical factor", by which is meant a measurable value of a physical property of the composition which is adversely affected by UV light. Examples of physical properties which may be adversely affected by TiO_2 and/or ZnO induced free radical attack include degradation and, in
30 consequence, strength, colour change e.g. for paints and textiles and photographic

-15-

stability e.g. for photographic films.

Thus if the rate of deterioration of a physical factor is X then the amount of the component(s) which is degraded possesses a said rate of deterioration of Y where Y is greater than X, preferably by at least 5%, and the amount of doped TiO₂ and/or ZnO and/or reduced ZnO reduces the said rate of loss from Y to X. The present invention also provides the use of a doped TiO₂/ZnO and/or reduced ZnO to reduce the rate of deterioration of a physical property of a polymeric composition or of an ingredient thereof. The present invention further provides a method of improving the stability of a physical property of a composition which comprises one or more components which are degraded by TiO₂ or ZnO or of such a component which comprises incorporating into the composition a doped TiO₂/ZnO and/or reduced ZnO.

The rate of colour change can be determined by illuminating a sample of the composition with and without the doped TiO₂ or ZnO or reduced ZnO with sunlight or visible light and measuring the spectral response of the composition over a given period and determining the change in wavelength emitted. Accelerated ageing tests using, for example a Fadeometer, can be used for this purpose.

The rate of loss of strength of an article of the present invention can be determined in a similar manner by measuring tensile properties such as the elongation at break or Young's modulus using standard equipment such as an Instron tester; again an accelerated ageing procedure is beneficial.

While any reduction in the wavelength change or other physical factor is an advantage, it is generally desirable that the presence of the doped oxide reduce the rate of change by an amount of at least 5%, preferably at least 10%, more preferably at least 15%, especially at least 20% and most preferably at least 40%.

In the polymeric compositions the metal oxides are preferably present at a concentration of about 0.5 to 20 % by weight, preferably about 1 to 10 % by weight and more preferably about 3 to 8 % by weight.

The dopant for the oxide particles is preferably manganese, which is especially preferred, e.g. Mn²⁺ but especially Mn³⁺, vanadium, for example V³⁺ or V⁵⁺,

-16-

chromium and iron but other metals which can be used include nickel, copper, tin, aluminium, lead, silver, zirconium, zinc, cobalt, gallium, niobium, for example Nb^{5+} , antimony, for example Sb^{3+} , tantalum, for example Ta^{5+} , strontium, calcium, magnesium, barium, molybdenum, for example Mo^{3+} , Mo^{5+} or Mo^{6+} as well as
5 silicon. Manganese is preferably present as Mn^{3+} , cobalt as Co^{2+} , tin as Sn^{4+} as well as Mn^{2+} . These metals can be incorporated singly or in combination of 2 or 3 or more. Further details of these doped oxides can be found in WO99/60994 as well as WO01/40114.

The optimum amount of the second component in the host lattice may be
10 determined by routine experimentation but it is preferably low enough so that the particles are not coloured. Amounts as low as 0.1 mole % or less, for example 0.05 mole %, or as high as 1 mole % or above, for example 5 mole % or 10 mole %, can generally be used. Typical concentrations are from 0.5 to 2 mole % by weight.

These particles can be obtained by any one of the standard processes for
15 preparing doped oxides and salts. Thus they can be obtained by a baking technique by combining particles of a host lattice (TiO_2/ZnO) with a second component in the form of a salt such as a chloride or an oxygen-containing anion such as a perchlorate or a nitrate, in solution or suspension, typically in solution in water, and then baking it, typically at a temperature of at least 300°C. Other routes which may be used to
20 prepare the doped materials include a precipitation process of the type described in J. Mat. Sci. (1997) 36, 6001-6008 where solutions of the dopant salt and of an alkoxide of the host metal (Ti/Zn) are mixed, and the mixed solution is then heated to convert the alkoxide to the oxide. Heating is continued until a precipitate of the doped material is obtained. Further details of preparation can be found in the aforesaid
25 patent specifications.

The rutile form of titania is known to be more photostable than the anatase form and is therefore preferred.

Reduced zinc oxide particles (i.e. particles which possess an excess of zinc ions relative to the oxygen ions) may be readily obtained by heating zinc oxide
30 particles in a reducing atmosphere to obtain reduced zinc oxide particles which

-17-

absorb UV light, especially UV light having a wavelength below 390 nm, and re-emit in the green, preferably at about 500 nm. It will be understood that the reduced zinc oxide particles will contain reduced zinc oxide consistent with minimising migration to the surface of the particles of electrons and/or positively charged holes such that
5 when said particles are exposed to UV light in an aqueous environment the production of hydroxyl radicals is substantially reduced as discussed above.

The reducing atmosphere can be air with a reduced oxygen content or an increased hydrogen content but is preferably a mixture of hydrogen and an inert gas such as nitrogen or argon. Typically the concentration of hydrogen is from 1 to 20%,
10 especially 5 to 15%, by volume, with the balance inert gas, especially nitrogen. A preferred reducing atmosphere is about 10% hydrogen and about 90% nitrogen by volume. The zinc oxide is heated in this atmosphere at, say, 500° to 1000°C, generally 750 to 850°C, for example about 800°C, for 5 to 60 minutes, generally 10 to 30 minutes. Typically it is heated to about 800°C for about 20 minutes.

15 It is believed that the reduced zinc oxide particles possess an excess of Zn^{2+} ions within the absorbing core. These are localised states and as such may exist within the band gap. A further discussion of this can be found in WO 99/60994.

The average primary particle size of the particles is generally from about 1 to 200 nm, for example about 1 to 150 nm, preferably from about 1 to 100 nm, more
20 preferably from about 1 to 50 nm and most preferably from about 20 to 50 nm. The particle size is preferably chosen to avoid colouration of the final product. Thus nanoparticles are frequently used. However, in one embodiment slightly larger particles for example from 100 to 500 nm, typically 100 to 400 or 450 nm especially from 150 to 300 nm and particularly 200 to 250 nm, can be employed. These provide
25 good coverage of, for example, skin imperfections without unacceptable skin whitening.

Where particles are substantially spherical then particle size will be taken to represent the diameter. However, the invention also encompasses particles which are non-spherical and in such cases the particle size refers to the largest dimension.

30 The oxide particles used in the present invention may have an inorganic or

-18-

organic coating. For example, the particles may be coated with oxides of elements such as aluminium, zirconium or silicon, especially silica. The particles of metal oxide may also be coated with one or more organic materials such as polyols, amines, alkanolamines, polymeric organic silicon compounds, for example,

- 5 $\text{RSi}[\{\text{OSi}(\text{Me})_2\}_x\text{OR}^1]_3$, where R is $\text{C}_1\text{-C}_{10}$ alkyl, R^1 is methyl or ethyl and x is an integer of from 4 to 12, hydrophilic polymers such as polyacrylamide, polyacrylic acid, carboxymethyl cellulose and xanthan gum or surfactants such as, for example, TOPO. Such coatings can have the effect of masking, at least to some extent, any colour which the doped particles may have.